

## STAR POLYMERS IN CORRELATED DISORDER

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We analyze the impact of a porous medium (structural disorder) on the scaling of the partition function of a star polymer immersed in a good solvent. We show that corresponding scaling exponents change if the disorder is long-range-correlated and calculate the exponents in the new universality class. A notable finding is that star and chain polymers react in *qualitatively* different manner on the presence of disorder: the corresponding scaling exponents *increase* for chains and *decrease* for stars. We discuss the physical consequences of this difference.

*Keywords:* polymers; polymer networks; quenched disorder; scaling laws.

### 1. Introduction

Polymer theory may serve as an archetype of an approach where the application of the path integral formalism leads both to a quantitative understanding of a whole range of physical, chemical, and biological phenomena

as well as to their accurate quantitative description.<sup>1-3</sup> Most directly this is shown by the Edwards model that describes a polymer chain in terms of a path integral and takes into account chain connectivity and self-avoiding interaction.<sup>3</sup> A textbook derivation maps this simple two-parameter model to the  $m = 0$  de Gennes limit<sup>4</sup> of the  $O(m)$  symmetric field theory. Standard field theoretical tools explain the origin of the scaling laws that govern polymer structural behaviour and allow to calculate the exponents that govern these scaling laws with high accuracy.

One of the generalizations of the above approach extends the theory to describe polymers of complex structure that form networks of interconnected polymer chains.<sup>5</sup> The intrinsic exponents that govern the scaling of a polymer network are uniquely defined by those of its constituents, star-like subunits known as star polymers<sup>6</sup> (see Fig. 1). The exponents that

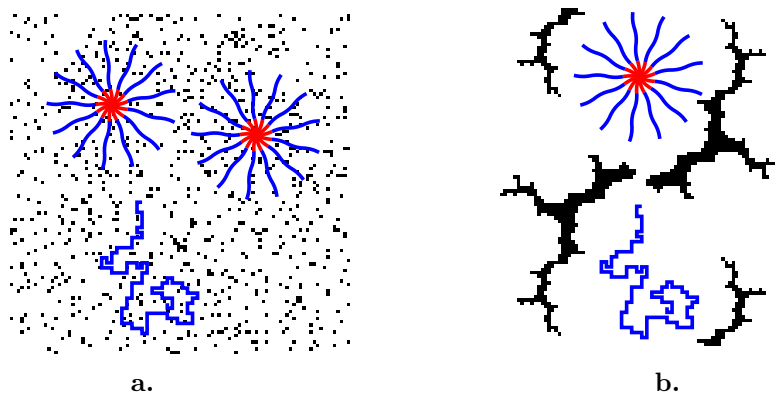


Fig. 1. Solution of star and chain polymers (blue on-line) in a good solvent immersed in a porous medium (black). We consider the disorder that characterizes pores (impurities) distribution as uncorrelated (a) or correlated (b). For the  $d$ -dimensional system, disorder is called long range correlated if the impurity-impurity pair correlation function decays for the large distances  $r$  as  $g(r) \sim r^{-a}$  with  $a < d$ .

govern the scaling of star polymers are universal in that they depend on space dimension  $d$  and star functionality  $f$  only (the number of chains attached to a common center).<sup>a</sup> Currently, star polymers are synthesized with high functionalities and form well-defined objects with interesting industrial, technological, and experimental applications.<sup>7</sup>

<sup>a</sup>Note, that for  $f = 1, f = 2$  a chain polymer is recovered.

In this paper we attract attention to another recent development in the analysis of the scaling properties of branched polymers.<sup>8,9</sup> Our analysis concerns the impact of structural disorder on the scaling of polymer stars and chains. For lattice models, where polymers are viewed as self-avoiding walks (SAW) this type of disorder may be realized by forbidding the SAW to visit certain lattice sites, which might be interpreted as lattice dilution. For real polymers in solvents, structural disorder may be implemented by filling a porous medium by a solvent with immersed polymers as shown in Fig. 1. As follows from our analysis sketched below, for long-range-correlated disorder the polymer behaviour displays a new universality, different from that of a SAW on a regular (undiluted) lattice. A notable consequence is that star and chain polymers react in *qualitatively* different manner on the presence of disorder: the corresponding scaling exponents *increase* for the chains and *decrease* for the stars. We discuss to which physical consequences such a difference in behaviour may lead.

## 2. Model and method

The starting point of our analysis is the Edwards continuous chain model, generalized to describe a branched polymer structure, a star polymer. We describe the conformation of each arm of the star by a path  $\mathbf{r}_a(s)$ , parameterized by  $0 \leq s \leq S_a$ ,  $a = 1, 2, \dots, f$  ( $S_a$ , the Gaussian surface of the  $a$ -th arm is related to the contour length of the chain),  $\mathbf{r}_a(0)$ , corresponds to the central point. The partition function of the system is defined by the path integral:<sup>5</sup>

$$\mathcal{Z}\{S_a\} = \int D[\mathbf{r}_1, \dots, \mathbf{r}_f] \exp \left[ -\frac{H_f}{k_B T} \right] \prod_{a=2}^f \delta^d(\mathbf{r}_a(0) - \mathbf{r}_1(0)). \quad (1)$$

Here, the product of  $\delta$ -functions ensures the star-like configuration of the set of  $f$  polymer chains described by the Hamiltonian:

$$\frac{H_f}{k_B T} = \frac{1}{2} \sum_{a=1}^f \int_0^{S_a} ds \left( \frac{d\mathbf{r}(s)}{ds} \right)^2 + \frac{u_0}{4!} \sum_{a,b=1}^f \int_0^{S_a} ds \int_0^{S_b} ds' \delta^d(\mathbf{r}_a(s) - \mathbf{r}_b(s')). \quad (2)$$

The first term in the r.h.s. of (2) presents chain connectivity whereas the second term describes an excluded volume interaction. Instead of introducing structural disorder directly into Eq. (1), we make use of its field theoretical representation. The corresponding derivations are described in details in Refs.<sup>5,8</sup> The relevant steps read:

(i) we map the continuous chain model (1) onto the  $m = 0$  limit of  $O(m)$

symmetric field theory by a familiar Laplace transform<sup>1</sup> in the Gaussian surface variables  $S_a$  to conjugated chemical potentials (mass variables)  $\mu_a$ . In this procedure, the product of  $\delta$ -functions in (1) is represented by a composite operator of a product of  $f$   $m$ -component fields

$$\sum_{\{k\}} \sum_{i_1, \dots, i_f=1}^m N^{i_1, \dots, i_f} \phi_{k_1}^{i_1} \dots \phi_{k_f}^{i_f}. \quad (3)$$

Here,  $N^{i_1, \dots, i_f}$  is a traceless tensor,  $\phi^i$  is an  $i$ -th component of the  $m$ -vector field  $\vec{\phi}$  and in the sum over wave vectors  $\{k\}$  is restricted by momentum conservation;

(ii) we introduce quenched random-temperature-like disorder shifting  $\mu_a \rightarrow \mu_a + \delta\mu_a(x)$  by random variables  $\delta\mu_a(x)$ . These have zero mean and correlations that decay at large distances as a power law:<sup>11</sup>

$$\langle \delta\mu_a(x) \delta\mu_a(y) \rangle \sim |x - y|^{-a}. \quad (4)$$

Here,  $\langle \dots \rangle$  stands for the configurational average over spatially homogeneous and isotropic disorder and the exponent  $a$  governs the correlation decay. As seen below, this leads to long range correlated disorder effects for  $a < d$ ;

(iii) to perform the configurational average of the free energy, we make use of the replica method resulting in field theoretical Lagrangean of two couplings  $u_0, w_0$ :

$$\begin{aligned} \mathcal{L} = & \frac{1}{2} \sum_{\alpha=1}^n \sum_k (\mu_0^2 + k^2) (\vec{\phi}_k^\alpha)^2 + \frac{u_0}{4!} \sum_{\alpha=1}^n \sum_{\{k\}} \left( \vec{\phi}_{k_1}^\alpha \cdot \vec{\phi}_{k_2}^\alpha \right) \left( \vec{\phi}_{k_3}^\alpha \cdot \vec{\phi}_{k_4}^\alpha \right) + \\ & \frac{w_0}{4!} \sum_{\alpha, \beta=1}^n \sum_{\{k\}} |k_1 + k_2|^{a-d} \left( \vec{\phi}_{k_1}^\alpha \cdot \vec{\phi}_{k_2}^\alpha \right) \left( \vec{\phi}_{k_3}^\beta \cdot \vec{\phi}_{k_4}^\beta \right). \end{aligned} \quad (5)$$

Note that the evaluation of the theory (5) involves a simultaneous polymer ( $m = 0$ ) and replica ( $n = 0$ ) limit. It is this anticipated double limit that allows us<sup>8</sup> to write the Lagrangean in terms of two coupling only. A third coupling appears<sup>11</sup> for  $m \neq 0$ .

We apply the field theoretical renormalization group (RG) approach to extract the universal content of (5). In this approach, the change of the couplings  $u, w$  under renormalization defines a flow in parametric space, governed by corresponding  $\beta$ -functions  $\beta_u(u, w)$ ,  $\beta_w(u, w)$ . The fixed points (FPs)  $u^*, w^*$  of this flow are the solutions to the system of equations:  $\beta_u(u^*, w^*) = 0$ ,  $\beta_w(u^*, w^*) = 0$ . If a stable FP exists and is accessible, it determines the scaling behaviour of the polymer system. In particular,

for a single polymer star of  $f$  arms of equal length  $N$  in a good solvent the partition sum (number of possible configurations) scales as

$$Z_{N,f} \sim e^{\mu N f} N^{\gamma_f - 1}, \quad N \rightarrow \infty, \quad (6)$$

with a non-universal fugacity  $e^\mu$  and the universal star exponent  $\gamma_f$ .<sup>6</sup> The latter is uniquely defined by the stable FP value of the anomalous dimension associated with the composite operator (3). We make use of two complementary perturbation theory expansions to calculate coordinates of the FPs and values of the exponents. In a first approximation we apply an expansion in<sup>11</sup>  $\varepsilon = 4 - d$  and  $\delta = 4 - a$  which allows for a qualitative description of the phenomena. In a further approach we apply perturbation theory in the renormalized couplings  $u$  and  $w$  evaluated at fixed dimension  $d = 3$  for a series of fixed values of the correlation parameter  $a$ .<sup>12</sup> In the latter case we proceed within a two-loop approximation refining the analysis by a resummation of the divergent RG series (see Ref.<sup>8-10</sup> for details). The FP picture that arises from our calculations is shown qualitatively in Fig. 2. Both calculation schemes display a range  $a_{\text{lower}}(d) < a < a_{\text{upper}}(d)$ , of

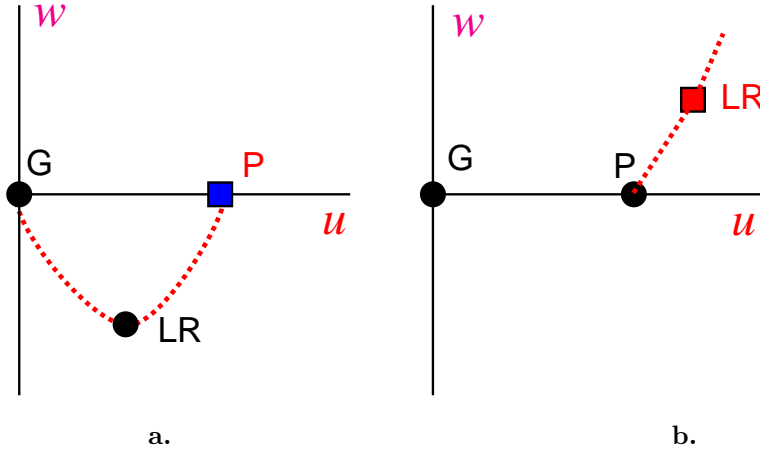


Fig. 2. Fixed points G (gaussian), P (pure) and LR (long range) of the RG flow in the plane of the two couplings  $u, w$ . The stable FP is shown by a square. (a) uncorrelated disorder  $a > d$ : P ( $u \neq 0, w = 0$ ) is stable. (b) correlated disorder  $a < d$ : LR ( $u \neq 0, w \neq 0$ ) is stable. Crossover occurs at  $a = d$  (c.f. Fig. 1).

values for  $a$  where the long-range-correlated FP (LR,  $u \neq 0, w \neq 0$ ) is stable and governs polymer scaling. For  $a < a_{\text{lower}}$ , no stable FP is found. This has been interpreted<sup>8</sup> as a collapse of a polymer coil for strongly cor-

related disorder. For  $a > a_{\text{upper}}$  the pure FP (P,  $u \neq 0$ ,  $w = 0$ ) is stable and polymer scaling is not perturbed by disorder. As far as power counting implies that the  $w$ -term in (5) is irrelevant in the RG sense for  $a \geq d$  it is natural to identify  $a_{\text{upper}} = d$ . Nonetheless, in first order approximation of the  $\varepsilon, \delta$ -expansion one finds that the LR FP is stable in the unphysical region  $d < a < 2 + d/2$ . Our two-loop calculations at fixed  $d, a$  for  $d = 3$  however result in  $a_{\text{upper}} = 3 = d$ ,  $a_{\text{lower}} = 2.2$  allowing for direct physical interpretations.

### 3. Scaling exponents

Qualitatively, the impact of disorder can be seen already from the first order  $\varepsilon, \delta$  results. Comparing the  $\gamma_f$  exponent (6) for the cases when the structural disorder is absent (or is short-range-correlated, Fig. 1a),<sup>6</sup>  $\gamma_f^{(0)} = 1 - \varepsilon f(f-3)/16$ , and when it is long-range-correlated (Fig. 1b),<sup>9</sup>  $\gamma_f^{(\delta)} = 1 - \delta f(f-3)/8$  we find:

$$\Delta\gamma_f \equiv \gamma_f^{(\delta)} - \gamma_f^{(0)} = \frac{f(f-3)}{16}(\varepsilon - 2\delta), \quad \varepsilon/2 < \delta < \varepsilon. \quad (7)$$

As one can see from this estimate, the exponent difference changes sign at

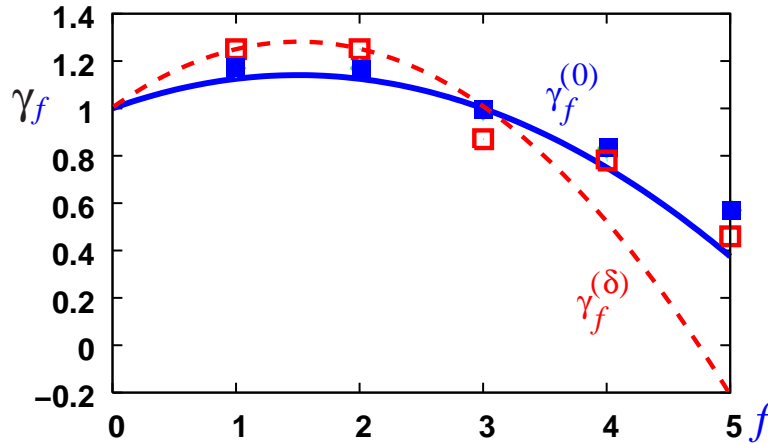


Fig. 3. Exponent  $\gamma_f$  of 3D polymer stars with  $f$  arms in a good solvent. Solid lines and filled squares indicate uncorrelated disorder, dashed lines  $\delta = 1.1$  and open squares  $a = 2.9$  correlated disorder; lines: first order  $\varepsilon, \delta$ -results; open, resp. filled, squares: second, resp. third, order resummed results for fixed  $d, a$ .

$f_{\pm} = 3$ . The two-loop calculations slightly shift this result towards  $f_{\pm} \leq 3$

while otherwise confirming the overall picture with more accurate numerical values for the exponents.<sup>9,10</sup> In Fig. 3 we plot the first order  $\varepsilon, \delta$ -curves for  $\gamma_f$  together with the resummed two-loop estimates for  $d = 3$ . A complete account of the numerical values of the exponents is given in Ref.<sup>9</sup> A prominent feature that follows from these results is that the effect of long-range-correlated disorder on polymer chains and polymer stars is qualitatively different. Whereas correlated disorder leads to an *increase* of  $\gamma_f$  for chain polymers (i.e. for  $f = 1, f = 2$ ), the same type of disorder *decreases* the  $\gamma_f$  exponent for the proper star polymers ( $f \geq 3$ ). Below we discuss some possible consequences of this difference. For  $f > 2$  we also observe that  $\gamma_f$  decreases monotonically as function of  $f$  for any valid value of  $a$  in the same way as it does for polymers in a good solvent:  $\gamma_{f_1}^{(a)} > \gamma_{f_2}^{(a)}$  for  $2 < f_1 < f_2$ . Furthermore, within the accuracy the data confirms a convexity from below of this function for valid values of  $a$  as well as for the  $\varepsilon, \delta$  expansion. The latter property ensures that polymer stars remain mutually repulsive in correlated disorder.<sup>13,14</sup>

#### 4. Conclusions and outlook

It has been recognized by now that star exponents come into play for the qualitative description and quantitative of different phenomena, where statistics of branched self avoiding and random walks is involved. The examples of such phenomena include short-range interaction of branched polymers in a good solvent),<sup>15</sup> diffusion-controlled reactions in the presence of polymers,<sup>16</sup> and, more generally, they are part of a multifractal description of diffusion limited growth in a Laplacian field.<sup>17</sup> Recently, star exponents have been used to estimate the thermal denaturation transition of DNA.<sup>18</sup> Our analysis opens a way to consider the impact of long-range-correlated disorder on the above phenomena.

A somewhat surprising effect that results from our calculations concerns the static separation in a solution of diluted chains and star polymers of equal molecular weight inside a porous medium. Following the estimates of the star exponents we predict that in a correlated medium star polymers will exert a higher osmotic pressure than chain polymers and in general higher branched star polymers will be expelled more strongly from the correlated porous medium. On the opposite, polymer chains will prefer a stronger correlated medium to a less or uncorrelated medium of the same density.<sup>9</sup>

A generalization of our approach to the case of star polymers built from chains of different species<sup>14</sup> will be presented elsewhere.<sup>19</sup>

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## References

1. J. des Cloizeaux and G. Jannink, *Polymers in Solution* (Clarendon Press, Oxford, 1990).
2. H. Kleinert, *Path Integrals in Quantum Mechanics, Statistics and Polymer Physics* (World Scientific, Singapore, 1995).
3. L. Schäfer, *Universal Properties of Polymer Solutions as Explained by the Renormalization Group* (Springer, Berlin, 1999).
4. P.-G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca and London, 1979).
5. L. Schäfer, C. von Ferber, U. Lehr, and B. Duplantier, *Nucl. Phys. B* **374**, 473 (1992).
6. B. Duplantier, *J. Stat. Phys.* **54**, 581 (1989).
7. G.S. Grest, L.J. Fetters, J.S. Huang, and D. Richter, *Adv. Chem. Phys.* **XCIV**, (1996); C. N. Likos, *Phys. Rep.* **348**, 267 (2001); *Star Polymers* Ed. by C. von Ferber and Yu. Holovatch (*Condens. Matter Phys.* **5** pp. 1-305, 2002).
8. V. Blavats'ka, C. von Ferber, and Yu. Holovatch, *Phys. Rev. E* **64**, 041102 (2001); *J. Phys.: Condens. Matter* **14**, 9465 (2002).
9. V. Blavats'ka, C. von Ferber, and Yu. Holovatch, *Phys. Rev. E* **74**, 031801 (2006).
10. V. Blavats'ka, C. von Ferber, R. Folk, and Yu. Holovatch, *Renormalization group approaches to polymers in disordered media*, pp.103-147 in: *Statistics of Linear Polymers in Disordered Media* Ed. by Bikas K. Chakrabarti (Elsevier, Amsterdam, 2005).
11. A. Weinrib and B.I. Halperin, *Phys. Rev. B* **27**, 417 (1983).
12. V. V. Prudnikov, P. V. Prudnikov, and A. A. Fedorenko, *J. Phys. A* **32**, L399 (1999); *J. Phys. A* **32**, 8587 (1999); *Phys. Rev. B* **62**, 8777 (2000).
13. B. Duplantier and A. W. Ludwig *Phys. Rev. Lett.* **66**, 247 (1991).
14. C. von Ferber and Yu. Holovatch, *Europhys. Lett.* **39**, 31 (1997); *Phys. Rev. E* **56**, 6370 (1997).
15. M. Watzlawek, C. N. Likos, and H. Löwen, *Phys. Rev. Lett.* **82**, 5289 (1999); C. von Ferber, Yu. Holovatch, A. Jusufi, C. N. Likos, H. Löwen, and M. Watzlawek, *Journ. Mol. Liq.* **93**, 151 (2001).
16. T. Witten and M. Cates, *Science* **232**, 1607 (1986); C. von Ferber and Yu. Holovatch, *Journ. Mol. Liq.*, **93**, 155 (2001).
17. M. E. Cates and T. A. Witten, *Phys. Rev. A* **35**, 1809 (1987); C. von Ferber and Yu. Holovatch, *Phys. Rev E* **59**, 6914 (1999).
18. Y. Kafri, D. Mukamel, and L. Peliti *Phys. Rev. Lett.* **85**, 4988 (2000); E. Carlon, E. Orlandini, and A. Stella, *Phys. Rev. Lett.* **88**, 198101 (2002).
19. V. Blavats'ka, C. von Ferber, and Yu. Holovatch, *in preparation* (2007)